

Properties of monovacancies and self-interstitials in bcc Li: An *ab initio* pseudopotential study

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The formation energy E_{1V}^F and the structural relaxation for a vacancy in bcc Li are calculated within the framework of the local-density approximation and the *ab initio* pseudopotential method for supercells, thereby correcting a small error in the pseudopotential used in former calculations. The calculated value of $E_{1V}^F=0.54$ eV is nearly identical to the activation energy for self-diffusion, suggesting an extraordinarily small vacancy-migration energy or a nonvacancy mechanism of self-diffusion. The results for self-interstitials exclude an interstitialcy mechanism. A local relaxation volume of -0.51 atomic volumes was found for the vacancy.

It is generally believed that self-diffusion in crystals uses lattice defects as vehicles. However, whereas in fcc and hcp metals as well as in bcc iron the monovacancy mechanism is confirmed to be dominant, the experimental evidence on Li and Na support the direct exchange of two atoms on adjacent lattice sites as the dominant self-diffusion mechanism.¹ In this paper we provide additional theoretical support for this statement from an *ab initio* calculation of the properties of monovacancies in Li crystals. It will be shown that the calculated vacancy-formation energy E_{1V}^F is very close to the experimentally obtained activation energy for self-diffusion E^{SD} . This demonstrates that either the vacancy-migration energy E_{1V}^M is extraordinarily small ($E_{1V}^M=E^{SD}-E_{1V}^F$), or that a nonvacancy mechanism is responsible for self-diffusion.

Recently the properties of monovacancies in bcc Li were studied² within the local-density approximation (LDA) by means of the *ab initio* pseudopotential method, taking into account the structural relaxation of the atoms surrounding the vacancy. Contrary to the general experience with the local-density approximation, the calculated lattice parameter a_0 of a perfect bcc Li crystal thereby was slightly larger than the experimental value. In the meantime, a small error in the pseudopotential used in the calculations was found. Because highly accurate values for the vacancy-formation energy are essential for the interpretation of the self-diffusion mechanism, we have redone the calculations with the correct pseudopotential. We will compare the new results with those of Ref. 2 and with those obtained by Benedek *et al.*³

The pseudopotential was constructed according to Hamann, Schlüter, and Chiang⁴ with a reference configuration $2s^{0.5}2p^{0.4}3d^{0.1}$ and $r_{c,s}=r_{c,p}=r_{c,d}=1.2$ a.u. as in Ref. 2. The cutoff radius r_{pc} for the partial-core correction⁵ was chosen in such a way that for $r=r_{pc}$ the core charge density was nine times the valence charge density, and the cutoff radius q_{max} for the pseudopotential in Fourier space was 7.9 [a.u.]⁻¹. The transferability of the pseudopotential was tested for several excited states, and the excitation energies computed with the pseudopotential agreed with the all-electron results within 10^{-4} Ry. The cohesive properties of the perfect lattice are given in Table I as determined with an energy

cutoff $E_c=20.5$ Ry and with $n_1=240$ k points in the irreducible Brillouin zone, the results being converged with respect to the parameters r_{pc} , q_{max} , E_c and n_1 . The data are compared with those from the pseudopotential (PS) calculations, the slightly defective one of Ref. 2 and the one of Benedek *et al.*³ based on a slightly different pseudopotential cast in Kleinman-Bylander form,⁶ as well as with the results from the full-potential linear-augmented-plane-wave calculation (FLAPW) in LDA of Perdew *et al.*⁷ and with the experimental data. Our results agree excellently with those from the FLAPW calculations. As expected, the lattice constant is slightly underestimated and the bulk modulus and cohesive energy are overestimated by the LDA.

The vacancy-formation energy E_{1V}^F was calculated by a supercell method² according to

$$E_{1V}^F = E(N-1, 1, V') - \frac{N-1}{N} E(N, 0, N\Omega_0), \quad (1)$$

where $E(N-1, 1, V')$ denotes the energy of a supercell with $N-1$ atoms and one vacancy at volume V' and $E(N, 0, N\Omega_0)$ is the energy of an ideal supercell with N atoms and volume $N\Omega_0$. Supercells with $N=16$ and $N=54$ have been used. The relaxation of the atoms around the vacancy was performed in two steps. First, a structural relaxation was made with the lattice constant of the ideal supercell. The atoms were moved according to the Hellmann-Feynman forces until the forces were zero. The result for the displacements of the individual

TABLE I. Results for the equilibrium lattice constant a_0 and volume Ω_0 , the bulk modulus B , and the cohesive energy E_{coh} of the ideal bcc structure of Li, in comparison with other theoretical and experimental data.

| | a_0 (Å) | B_0 (Mbar) | E_{coh} (eV) | Ω_0 (Å ³) |
|----------------------|-----------|--------------|----------------|------------------------------|
| This paper | 3.356 | 0.152 | -1.72 | 18.90 |
| PS (Ref. 2) | 3.534 | 0.133 | -1.48 | 22.07 |
| PS (Ref. 3) | 3.280 | | | 17.64 |
| FLAPW (Ref. 7) | 3.364 | 0.150 | | 19.03 |
| Experiment (Ref. 13) | 3.491 | 0.116 | -1.63 | 21.27 |

atoms (Fig. 1) is very similar to the one obtained in Refs. 2 and 3. In the second step, a volume relaxation was performed according to the prescription given in Ref. 2. This volume relaxation determines the local relaxation volume of the vacancy, but it affects the vacancy-formation energy as obtained from the supercell $N=54$ by less than 0.01 eV. It turned out that an additional structural relaxation after this volume relaxation affected the relative positions of the atoms only very slightly.

The results for the vacancy formation energy are presented in Table II for $N=16, 54$ and for various values of E_c and various numbers n of k points used for the Brillouin-zone sampling (corresponding to n_1 k points in the irreducible Brillouin zone of a one-atom unit cell). It turned out that there are significant differences between the present calculation and the former calculation using a slightly defective pseudopotential.² Nevertheless, the general behavior concerning the convergence with respect to N , E_c , and n is preserved, and therefore we also exhibit the results from Ref. 2 in parentheses.

It can be seen from Table II that the 16 atom supercell is too small to obtain reliable values for the formation energy. This finite-size effect is nearly entirely due to the relaxation of the atoms. If the relaxation is omitted, there is a fast convergence with respect to the supercell size (see also Refs. 8–10). This becomes obvious by comparing the results in parentheses for the unrelaxed $N=16$ and $N=54$ supercells, for $E_c=8.5$ Ry and $n_1=112$, which differ only by 0.02 eV. It therefore should be possible¹⁰ to calculate the “electronic part” of the vacancy-formation energy from small unrelaxed supercells and to correct for the “structural part” via elasticity theory or lattice statics.

Furthermore, Table II shows that for the case of Li the vacancy-formation energy, which, according to Eq. (1) is the difference between two total energies, converges rather rapidly with increasing E_c and n_1 , although the total energies themselves converge rather slowly. For instance, there is virtually no difference between the (relaxed) $N=54$ results (in parentheses) for $E_c=8.5$ Ry and

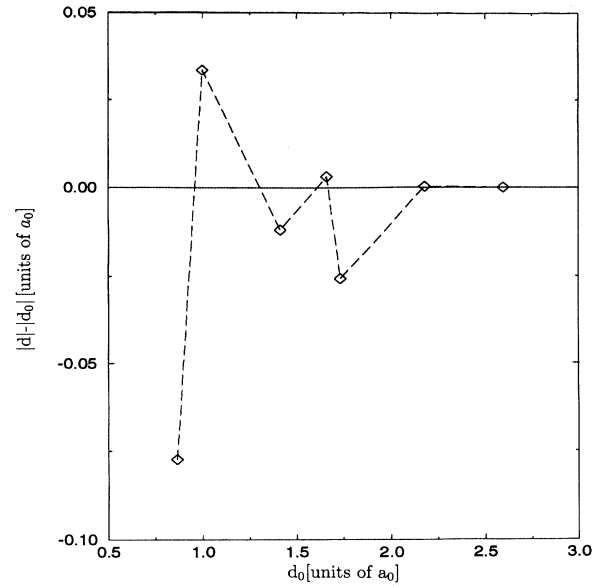


FIG. 1. Relaxation of the neighboring atoms around the vacancy. The figure shows the modification of the distance d from the vacancy as function of the original distance d_0 , in units of the original lattice constant a_0 .

$n_1=112$ or $n_1=728$. There is also no difference between the relaxed $N=54$ results (in parentheses) for $n_1=112$ and $E_c=8.5$ Ry or $E_c=10.5$ Ry. For the case of Al the convergence with respect to the number of k points is much slower.^{8–10}

Altogether, we think that our result for $N=54$, $E_c=10.5$ Ry, and $n_1=112$ represents the vacancy-formation energy in LDA with an accuracy of the order of about 0.01–0.02 eV. We arrive at $E_{1V}^F=0.54$ eV, which is considerably larger than the value of 0.47 eV found with the defective pseudopotential in Ref. 2 but rather close to the value of $E_{1V}^F=0.57$ eV found by

TABLE II. Results for the vacancy-formation energy E_{1V}^F for different values of N (number of sites in the supercell), E_c (cutoff energy for the plane-wave basis), the number n of k points in the irreducible Brillouin zone of the superlattice, and the corresponding number n_1 of k points in the irreducible Brillouin zone of a one-atom unit cell. The superscripts a and b denote high-symmetry and low-symmetry k points.

| N | E_c [Ry] | k points | | E_{1V}^F (eV) | |
|-----|------------|----------------|-------|--------------------|-----------------|
| | | n | n_1 | Without relaxation | With relaxation |
| 16 | 8.5 | 1 | 5 | 0.46 | 0.44 |
| | 8.5 | 4 | 14 | 0.75 | |
| | 8.5 | 10 | 112 | (0.74) | |
| | 8.5 | 4 | 14 | (0.54) | |
| 54 | 10.5 | 4 | 14 | 0.75 | 0.72 |
| | 8.5 | 1 | 8 | 0.81 | |
| | 8.5 | 4 ^a | 30 | (0.77) | |
| | 8.5 | 4 ^b | 112 | (0.60) | |
| | 8.5 | 20 | 728 | (0.56) | |
| | 8.5 | 4 ^a | 30 | (0.56) | |
| | 10.5 | 4 ^a | 30 | 0.60 | |
| | 10.5 | 4 ^b | 112 | 0.54 | |

Benedek *et al.*³ for a relaxed $N=54$ supercell calculation on the basis of a slightly different pseudopotential cast in Kleinman-Bylander form and with one special k point in the Brillouin zone of the supercell ($n=1$).

Our calculated value for E_{1V}^F is nearly identical to the experimental low-temperature value¹¹ for the activation energy of self-diffusion, $E^{SD}=0.52\pm 0.02$ eV. This means that either the vacancy-migration energy is extraordinarily small, or that a nonvacancy mechanism is responsible for self-diffusion. Schultz¹⁴ has presented arguments in favor of a small migration energy, which, however, are either not unambiguous or purely empirical. We therefore have already started a calculation of the vacancy-migration energy with the *ab initio* pseudopotential method. During the search for a nonvacancy mechanism we also considered an interstitialcy mechanism for self-diffusion. To do this, the formation energy E_f^F was calculated^{10,12} for various self-interstitial configurations, viz. octahedral and tetrahedral interstitials, $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ dumbbells, and a configuration that might be the saddle-point configuration of the $\langle 111 \rangle$ crowdion. Unfortunately, most of the calculations were performed

with the defective pseudopotential. Nevertheless, we think that the basic result is correct, namely that the lowest formation energies are those for the $\langle 110 \rangle$ and $\langle 111 \rangle$ dumbbells, which are about 40% larger than E_{1V}^F for the fully relaxed $N=54$ supercell. In order to check the reliability of these results we have recalculated the (unrelaxed) formation energy of the $\langle 111 \rangle$ dumbbell with the correct pseudopotential for $N=16$, $E_c=10.5$ Ry, and $n_1=14$ and found a deviation of about 6%. We therefore think that an interstitialcy mechanism cannot be the dominant self-diffusion mechanism in Li. Calculations are under way to explore the possibility of a direct exchange between adjacent atoms as a self-diffusion mechanism in bcc Li.

Finally, we have calculated the *local* relaxation volume $\Delta V = V' - N\Omega_0$ for the supercell with $N=54$, $E_c=10.5$ Ry, and $n_1=30$. We obtained $\Delta V = -0.51\Omega_0$, which agrees well with the value of $\Delta V = -0.48\Omega_0$ found in Ref. 2.

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